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TITLE: LIQUID RAW MATERIAL SUPPLY DEVICE FOR CVD

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INVENTOR-INFORMATION:

NAME	COUNTRY
ONABE, KAZUNORI	N/A
SADAKATA, NOBUYUKI	N/A
SAITO, TAKASHI	N/A
NAGAYA, SHIGEO	N/A

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide a liquid raw material supply device for CVD
which is cost effective and is capable of reducing the dimensional differences occurring in the individual differences of the liquid raw material supply device and improving the reproducibility of the supply condition and atomization condition of liquid raw material.

SOLUTION: This liquid raw material supply device includes a capillary 31a as a raw material soln. supply section to be internally supplied with the liquid raw material, a capillary insertion section 31 into which the capillary 31a is inserted, an atomizing gas supply section 32 of a cylindrical and converging shape which is disposed to enclose the outer periphery of the capillary insertion section 31 and is supplied with an atomizing gas for atomizing the liquid raw material into the spacing between itself and the capillary insertion section 31 and a cylindrical shielding gas supply section 33 which is disposed to enclose the outer periphery of the atomizing gas supply section 32 and is supplied with a shielding gas for cooling and shielding the capillary 31a, the capillary insertion section 31 and the atomizing gas supply section 32 to the spacing between itself and the atomizing gas supply section 32. The capillary 31a is attachably and detachably and exchangeably inserted into the capillary

* NOTICES *

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2.**** shows the word which can not be translated.
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CLAIMS

[Claim(s)]
[Claim 1] The capillary tube insertion section in which the capillary tube and this capillary tube as a raw material solution feed zone by which a liquid raw material is supplied to the interior are inserted, The periphery of this capillary tube insertion section is surrounded, and it is prepared, and narrows the point in tubed [by which the atomize gus for atomizing said liquid raw material is supplied to the clearance between said capillary tube insertion sections]. The atomize gus feed zone of **, It comes to provide the tubed shielding gas feed zone by which the shielding gas which encloses the periphery of this atomize gus feed zone, is formed, and cools and shields said capillary tube, said capillary tube insertion section, and said atomize gus feed zone is supplied to the clearance between said atomize gus feed zones. said capillary tube -- attachment and detachment -- the liquid feeding equipment for CVD characterized by being inserted in said capillary tube insertion section exchangeable.
[Claim 2] Liquid feeding equipment for CVD according to claim 1 characterized by the bore of said capillary tube being 50 micrometers - 150 micrometers.
[Claim 3] Liquid feeding equipment for CVD according to claim 1 or 2 characterized by what the pressure type liquid pump for carrying out pressurization liquid sending possesses said liquid raw material for in said capillary tube.

[Translation done.]

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(71)出願人　000005186
株式会社フジクラ
東京都江東区木場１丁目５番１号

(71)出願人　000213297
中部電力株式会社
愛知県名古屋市東区東新町１番地

(72)発明者　尾鍋　和憲
東京都江東区木場１丁目５番１号　株式会社フジクラ内

(72)発明者　定方　伸行
東京都江東区木場１丁目５番１号　株式会社フジクラ内

(74)代理人　弁理士　志賀　正武　（外３名）

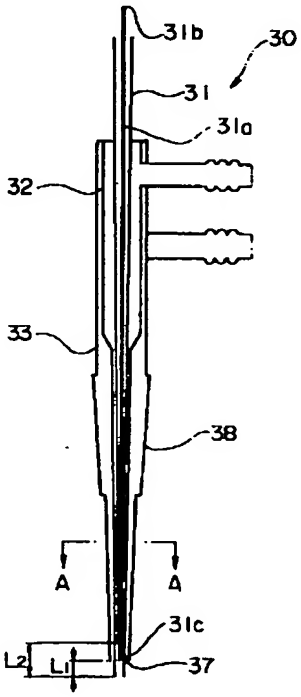
最終頁に続く

(54)【発明の名称】　ＣＶＤ用液体原料供給装置

(57)【要約】

【課題】　経済的であり、液体原料供給装置の個体差に起因する寸法差異を低減でき、液体原料の供給状況および霧化状況の再現性を向上できるＣＶＤ用液体原料供給装置の提供。

【解決手段】　内部に液体原料が供給される原料溶液供給部としての毛細管３１ａと、毛細管３１ａが挿入される毛細管挿入部３１と、毛細管挿入部３１の外周を取り囲んで設けられ、毛細管挿入部３１との隙間に液体原料を霧化するためのアトマイズガスが供給される筒状で先窄まり状のアトマイズガス供給部３２と、アトマイズガス供給部３２の外周を取り囲んで設けられ、毛細管３１ａと毛細管挿入部３１とアトマイズガス供給部３２を冷却ならびにシールドするシールドガスがアトマイズガス供給部３２との隙間に供給される筒状のシールドガス供給部３３を具備してなり、毛細管３１ａは着脱交換可能に毛細管挿入部３１ａに挿入されていることを特徴とするＣＶＤ用液体原料供給装置３０。



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【特許請求の範囲】

【請求項1】　内部に液体原料が供給される原料溶液供給部としての毛細管と、該毛細管が挿入される毛細管挿入部と、該毛細管挿入部の外周を取り囲んで設けられ、前記毛細管挿入部との隙間に前記液体原料を霧化するためのアトマイズガスが供給される筒状で先窄まり状のアトマイズガス供給部と、該アトマイズガス供給部の外周を取り囲んで設けられ、前記毛細管と前記毛細管挿入部と前記アトマイズガス供給部を冷却ならびににシールドするシールドガスが前記アトマイズガス供給部との隙間に供給される筒状のシールドガス供給部を具備してなり、前記毛細管は着脱交換可能に前記毛細管挿入部に挿入されていることを特徴とするＣＶＤ用液体原料供給装置。

【請求項2】　前記毛細管の内径が５０μｍ～１５０μｍであることを特徴とする請求項１記載のＣＶＤ用液体原料供給装置。

【請求項3】　前記液体原料を前記毛細管内に加圧送液するための加圧式液体ポンプが具備されたことを特徴とする請求項１または２記載のＣＶＤ用液体原料供給装置。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、化学気相蒸着法（以下、ＣＶＤ法という）によって酸化物超電導体などの酸化物材料を基材上に成膜する薄膜形成装置に備えられるＣＶＤ用液体原料供給装置に関するものである。

【０００２】

【従来の技術】近年、臨界温度（Ｔｃ）が液体窒素温度（約７７Ｋ）よりも高い酸化物超電導体として、例えば、Ｙ-Ｂａ-Ｃｕ-Ｏ系、Ｂｉ-Ｓｒ-Ｃａ-Ｃｕ-Ｏ系、Ｔｌ-Ｂａ-Ｃａ-Ｃｕ-Ｏ系などの酸化物超電導体が発見されている。そして、これらの酸化物超電導体は、電力ケーブル、マグネット、エネルギー貯蔵、発電機、医療機器、電流リード等の分野に利用する目的で種々の研究が進められている。このような酸化物超電導体の製造方法の１つとして、化学気相蒸着法（ＣＶＤ法）等の薄膜形成手段によって基材表面に酸化物超電導薄膜を成膜する方法が知られている。この種の薄膜形成手段により形成した酸化物超電導薄膜は、臨界電流密度（Ｊｃ）が大きく、優れた超電導特性を発揮することが知られている。また、ＣＶＤ法のなかでも、金属錯体、金属アルコキシドなどの有機金属化合物を原料として行なうＣＶＤ法は、成膜速度が速く、短時間でより厚い膜を形成できる手段として注目されている。

【０００３】このようなＣＶＤ法による酸化物超電導体の製造方法において通常使用される原料化合物としては、酸化物超電導体を構成する各元素のβ－ジケトン化合物やシクロペンタジエニル化合物などが用いられ、例えば、Ｙ-Ｂａ-Ｃｕ-Ｏ系の酸化物超電導体の製造用には、Ｙ（ｔｈｄ）$_3$、Ｂａ（ｔｈｄ）$_2$またはＢａ（ｔｈｄ）$_2$・ｐｈｅｎ$_2$、Ｃｕ（ｔｈｄ）$_2$等の有機金属錯体原料（ＭＯ原料）などが使用されている（ｔｈｄ＝2,2,6,6-ﾃﾄﾗﾒﾁﾙ-3,5-ﾍﾌﾟﾀﾝｼﾞｵﾝ）。これらの有機金属錯体原料は、室温で固体の原料であり、２００～３００℃に加熱することにより高い昇華特性を示すが、原料の純度や、加熱時間に伴う仕込み原料の表面積変化等により昇華効率が大きく左右されるために組成制御が困難であるが、これらの固体の錯体原料はテトラヒドロフラン（ＴＨＦ）、イソプロパノール、トルエン、ジグリム（2,5,8-ﾄﾘｵｷｿﾉﾅﾝ）等の有機溶媒に溶かして液体原料として用いられていた。

【０００４】これらの液体原料は、後述するようにさらに気化器で加熱気化させてキャリアガスとともに反応チャンバに送り込まれ、この反応チャンバ内で化学反応を生じさせ、反応チャンバ内に設置した基材の表面に反応生成物を堆積させることで目的のＹ-Ｂａ-Ｃｕ-Ｏ系酸化物超電導体を得ることができる。ところで、有機溶媒に有機金属錯体原料を溶解したものをＣＶＤ用液体原料として用いる場合に、そのＣＶＤ用液体原料供給装置が問題となっていた。

【０００５】上述のような酸化物超電導体の製造に用いられる従来のＣＶＤ用液体原料供給装置を備えた酸化物超電導体の製造装置としては、液体原料を貯留するとともに該原料溶液をＣＶＤ用液体原料供給装置に送液する原液供給装置と、送液された液体原料を気化器内に噴霧するＣＶＤ用液体原料供給装置と、噴霧された液体原料を気化させ、原料ガスとするとともにこの原料ガスをＣＶＤ反応装置内に供給する気化器と、供給された原料ガスを加熱されたテープ状の基上に堆積させるＣＶＤ反応装置から概略構成されている。

【０００６】上記ＣＶＤ用液体原料供給装置としては、本願発明者らにより特願平９－１４３７３８号のものが提案されている。このＣＶＤ用液体原料供給装置は、内部に液体原料が供給される筒状の原料溶液供給部と、該原料溶液供給部の外周を取り囲んで設けられ、上記原料溶液供給部との隙間に上記液体原料を霧化するためのアトマイズガスが供給される筒状で先窄まり状のアトマイズガス供給部と、該アトマイズガス供給部の外周を取り囲んで設けられ、上記アトマイズガス供給部との隙間に上記原料溶液供給部と上記アトマイズガス供給部を冷却ならびににシールドするシールドガスが供給される筒状のシールドガス供給部とから概略構成される３重管構造のものである。このＣＶＤ用液体原料供給装置は、ガラス製であり、該装置を構成するアトマイズガス供給部とシールドガス供給部とは互いに上端部で接合一体化されており、これらに上記原料溶液供給部が一体的に接合されている。このような構成のＣＶＤ用液体原料供給装置によれば、気化器内部にＴＨＦ等を溶媒とする蒸気圧の高い液体原料を比較的安定して連続供給が可能である。

【０００７】このような従来の液体原料供給装置（原料

溶液供給部一体型の液体原料供給装置）を備えた酸化物超電導体の製造装置を用いて長尺の酸化物超電導体を製造するには、原液供給装置から液体原料をＣＶＤ用液体原料供給装置の原料溶液供給部内に送液し、該供給部内に送液された液体原料を気化器内に噴霧し、該噴霧された液体原料を気化器内で気化させて原料ガスとし、この原料ガスをＣＶＤ反応装置内に供給する。これとともにＣＶＤ反応装置内にテープ状の基材を走行させ、さらに該テープ状の基材を加熱して反応生成物を基材上に堆積させることにより長尺の酸化物超電導体が得られる。

【０００８】

【発明が解決しようとする課題】しかしながら従来のＣＶＤ用液体原料供給装置においては、液体原料の供給量により原料溶液供給部の最適な内径が異なるため、酸化物超電導薄膜の成膜の際には、予め原料溶液供給部の内径が異なる数種類の液体原料供給装置を用意しておき、液体原料の供給量を変更する都度、最適な内径を有する原料溶液供給部を有する液体原料供給装置を選択し、原料溶液供給部の内径が不適切な場合には液体原料供給装置ごと取り替えなければならず、不経済であった。また、従来の液体原料供給装置は、手作りのガラス製品であるため、完全に同一寸法のものを作製するのが困難であり、原料溶液供給部の管径だけでなく、アトマイズガス供給部やシールドガス供給部の管径も微妙に異なってしまうため、装置毎に液体原料の供給状況が変化してしまい液体原料の供給状況および霧化状況の再現性が悪いという問題があった。従って、従来の液体原料供給装置が備えられた酸化物超電導体の製造装置を用いて酸化物超電導体を製造する場合に、液体原料供給装置を交換すると、該装置の個体差に起因する寸法誤差により、良好な酸化物超電導薄膜が再現性良く得られないという問題があった。

【０００９】本発明は上記事情に鑑みてなされたものであり、経済的であり、液体原料供給装置の個体差に起因する寸法差異を低減でき、液体原料の供給状況および霧化状況の再現性を向上できるＣＶＤ用液体原料供給装置を提供することを目的とする。

【００１０】

【課題を解決するための手段】請求項１記載の発明では、内部に液体原料が供給される原料溶液供給部としての毛細管と、該毛細管が挿入される毛細管挿入部と、該毛細管挿入部の外周を取り囲んで設けられ、上記毛細管挿入部との隙間に上記液体原料を霧化するためのアトマイズガスが供給される筒状で先窄まり状のアトマイズガス供給部と、該アトマイズガス供給部の外周を取り囲んで設けられ、上記毛細管と上記毛細管挿入部と上記アトマイズガス供給部を冷却ならびにシールドするシールドガスが上記アトマイズガス供給部との隙間に供給される筒状のシールドガス供給部を具備してなり、上記毛細管は着脱交換可能に上記毛細管挿入部に挿入されていることを特徴とするＣＶＤ用液体原料供給装置を上記課題の解決手段とした。

【００１１】また、請求項２記載の発明では、上記毛細管の内径が５０μｍ～１５０μｍであることを特徴とする請求項１記載のＣＶＤ用液体原料供給装置を上記課題の解決手段とした。また、請求項３記載の発明では、上記液体原料を上記毛細管内に加圧送液するための加圧式液体ポンプが具備されたことを特徴とする請求項１または２記載のＣＶＤ用液体原料供給装置を上記課題の解決手段とした。

【００１２】

【発明の実施の形態】以下、本発明のＣＶＤ用液体原料供給装置の一実施形態を図面を用いて説明する。図１は本発明に係るＣＶＤ用液体原料供給装置を備えた酸化物超電導体の製造装置の一例を示すものである。この酸化物超電導体の製造装置は、ＣＶＤ用液体原料供給装置３０と、原液供給装置４０と、気化器５０と、ＣＶＤ反応装置６０とから概略構成されている。

【００１３】液体原料供給装置３０は、図２から図３に示すように、内部に液体原料が供給される原料溶液供給部としての毛細管３１ａと、毛細管３１ａが挿入される毛細管挿入部３１と、毛細管挿入部３１の外周を取り囲んで設けられた筒状で先窄まり状のアトマイズガス供給部３２と、該アトマイズガス供給部３２の先端部を除いた外周を取り囲んで設けられた筒状のシールドガス供給部３３とから概略構成されたものである。

【００１４】毛細管３１ａは、原液供給装置４０から送り込まれてくる液体原料３４が内部に供給されるものである。毛細管３１ａの寸法の具体例としては、外径が３７５μｍ程度であり、内径が数１０μｍ～数百μｍ程度、より好ましい内径としては５０μｍ～１５０μｍ程度である。

【００１５】上述のような構成の毛細管３１ａは、着脱交換可能に毛細管挿入部３１に挿入されている。毛細管挿入部３１は、毛細管３１ａをアトマイズガス供給部３２内に案内するためのものである。毛細管挿入部３１の先端部の内径は、毛細管３１ａの外径に近い値であることが好ましい。毛細管３１ａの外径が３７５μｍの場合の毛細管挿入部３１の寸法の具体例としては、内径３８０μｍ～３９０μｍ程度、外径４２５～４７５μｍ程度とされる。このような毛細管挿入部３１内に挿入された毛細管３１ａは、後述する原液供給装置４０と接続されている。

【００１６】この毛細管３１ａの中央部には供給された液体原料３４を一時的に貯留する液だまり（図示略）が設けられていることが好ましい。この液だまりの内径は、毛細管３１ａの上部の液体供給口３１ｂや下部の液体供給口３１ｂの内径よりも大きくなっており、原液供給装置４０から送り込まれた液体原料３４が溜まりつつ連続的に先端に送り込まれるようになっている。このよ

うな液だまりが設けられていると、液体原料３４中に気泡等が混入していても、気泡等は液だまりに溜った液体原料３４の液面に浮き上がるため、先端にまで達するのを防止できる。

【００１７】上述のような数１０μm～数百μm程度の内径を有する毛細管３１ａ内に液体原料３４を送液するためには、数１０ｋｇ／ｃｍ²の送圧力が必要となるため、原液供給装置４０から送り込まれてくる液体原料３４を毛細管３１ａ内に加圧送液するための加圧式液体ポンプ３５が接続管３５ａを介して液体供給口３１ｂに接続されていることが好ましい。このような加圧式液体ポンプ３５が設けられていると、液体原料３４を数１００ｋｇ／ｃｍ²で加圧送液することができる。この加圧式液体ポンプ３５には、後述する原液供給装置４０が接続管４１を介して接続される。

【００１８】アトマイズガス供給部３２は、毛細管挿入部３１との隙間に上述の液体原料３４を霧化するためのアトマイズガスが供給されるものである。アトマイズガス供給部３２の上部には、アトマイズガス用ＭＦＣ３６ａを介してアトマイズガス供給源３６が接続され、アトマイズガス供給部３２内にアトマイズガスを供給できるように構成されている。ここで用いられるアトマイズガスの具体例を明示するならば、アルゴンガス、ヘリウムガス、窒素ガスなどである。

【００１９】シールドガス供給部３３は、毛細管３１ａと毛細管挿入部３１とアトマイズガス供給部３２を冷却するとともにノズル３７をシールドするためのシールドガスがアトマイズガス供給部３２との隙間に供給されるものである。シールドガス供給部３３の中央部より下方の部分には外方に突出するテーパ部３８が設けられている。また、シールドガス供給部３３の上部には、シールドガス用ＭＦＣ３９ａを介してシールドガス供給源３９が接続され、シールドガス供給部３３内にシールドガスを供給できるように構成されている。ここで用いられるシールドガスの具体例を明示するならば、アルゴンガス、ヘリウムガス、窒素ガスなどである。

【００２０】この液体原料供給装置３０は、ガラスなどからなるものであり、該装置３０を構成するアトマイズガス供給部３２とシールドガス供給部３３は互いに上端部で接合一体化されており、さらにこれらに毛細管挿入部３１が一体的に接合されている。そして、この例の液体原料供給装置３０では、アトマイズガス供給部３２の先端部と毛細管３１ａの先端部とからノズル３７が構成されている。アトマイズガス供給部３２の先端部は、シールドガス供給部３３の先端部より僅かに突出しており、ここでの突出長さL_1としては、例えば１ｍｍ程度である。また、アトマイズガス供給部３２の先端部は、毛細管挿入部３１の先端部より突出しており、ここでの突出長さL_2としては、例えば３ｍｍ程度である。一方、挿入する毛細管３１ａの先端は、アトマイズガス供給部３２の先端部に対し±１ｍｍの範囲で調節される（＋は毛細管３１ａの先端がアトマイズガス供給部３２の先端部より突出する場合であり、－は毛細管３１ａの先端がアトマイズガス供給部３２の先端部より引っ込んでいる場合である）。

【００２１】上述のような構成の液体原料供給装置３０では、液体原料３４を液体供給口３１ｂから毛細管３１ａ内に一定流量で圧送するとともにアトマイズガスをアトマイズガス供給部３２に一定流量で送り込むと、液体原料３４は毛細管３１ａの吐出口３１ｃに達するが、該先端の外側のアトマイズガス供給部３２の先端からアトマイズガスが流れてくるので、吐出口３１ｃから吹き出る際、液体原料３４は上記アトマイズガスにより直ちに霧化され、一定量のミスト状の液体原料３４を気化器５０内に連続的に供給することができるようになっている。また、これとともにシールドガスをシールドガス供給部３３に一定流量で送り込むと、アトマイズガス供給部３２と毛細管挿入部３１と毛細管３１ａが冷却されるので該毛細管３１ａ内を流れる液体原料３４も冷却され、該液体原料３４が途中で気化するのを防止できるようになっている。さらにまた、アトマイズガス供給部３２の先端の外側で、かつ上方のシールドガス供給部３３の先端からシールドガスが流れてくるので、該シールドガスによりノズル３７の周囲がシールドされ、気化器５０内で液体原料３４が気化した原料ガスがノズル３７に付着して固体原料となって再析出するのを防止できるようになっている。

【００２２】このような液体原料供給装置３０の毛細管３１ａには、液体原料用ＭＦＣ４１ａを備えた接続管４１と、加圧式液体ポンプ３５を備えた接続管３５ａを介して原液供給装置４０が接続されいる。これら接続管３５ａ、４１は、内面がフッ素樹脂でコートされたパイプなどの耐薬品性に優れたものが使用される。原液供給装置４０は、収納容器４２と、加圧源４３を具備し、収納容器４２の内部には液体原料３４が収納されている。収納容器４２は、ガラス瓶などの耐薬品性に優れたものが使用される。上記加圧源４３は、収納容器４２内にＨｅガス等を供給することにより収納容器４２内を加圧して収納容器４２内に満たされた液体原料３４を接続管４１に一定流量で排出できるようになっている。

【００２３】収納容器４２に収納されている液体原料３４は、成膜するべき目的化合物の構成金属元素の有機金属錯体、金属アルコキシドなどの金属有機化合物を、目的化合物の組成比となるように複数種混合して有機溶媒に溶解したものである。これらの金属有機化合物および有機溶媒の具体例を明示するならば、Y-Ba-Cu-O系酸化物超電導体を成膜する場合に用いられるＹ（ｔｈｄ）₃、Ｂａ（ｔｈｄ）₂またはＢａ（ｔｈｄ）₂・ｐｈｅｎ₂、Ｃｕ（ｔｈｄ）₂等（ｔｈｄ＝2,2,6,6-ﾃﾄﾗﾒﾁﾙ-3,5-ﾍﾌﾟﾀﾝｼﾞｵﾝ）の有機金属錯体、および、テトラヒド

ロフラン（THF）、イソプロパノール、トルエン、ジグリム（2,5,8-トリオキソノナン）などの有機溶媒である。

【0024】一方、液体原料供給装置30の下方には容器状の気化器50が配設されており、液体原料供給装置30の中央部から先端部が該気化器50内に収納されて液体原料供給装置30と気化器50とが接続されている。この気化器50の外周部には、気化器50の内部を加熱するためのヒータ51が付設されていて、このヒータ51により上記ノズル37から噴霧されたミスト状の液体原料34を所望の温度に加熱して気化させ、原料ガスが得られるようになっている。この気化器50は、輸送管53を介してCVD反応装置60に接続されている。

【0025】このCVD反応装置60は、石英製の反応チャンバ61を有し、この反応チャンバ61は、横長の両端を閉じた筒型のもので、隔壁（図示略）によって図1の左側から順に基材導入部62と反応生成室63と基材導出部64に区画されている。更に、基材導入部62にはテープ状の基材65を導入するための導入孔が形成されるとともに、基材導出部64には基材65を導出するための導出孔が形成されており、また、導入孔と導出孔の周縁部には、図面では省略されているが基材65を通過させている状態で各孔の隙間を閉じて基材導入部62と基材導出部64を気密状態に保持する封止部材が設けられている。また、反応生成室63の天井部には、反応生成室63に連通する三角型のガス拡散部66が取り付けられている。

【0026】一方、CVD反応装置60の外部には、基材導入部62の反応生成室63側方の部分から基材導出部64の反応生成室63側方の部分を覆う加熱ヒータ47が設けられ、基材導入部62が不活性ガス供給源68に、また、基材導出部64が酸素ガス供給源69にそれぞれ接続されている。また、ガス拡散部66には原料ガスの気化器50と接続された輸送管53が接続されている。この輸送管53の周囲には原料ガスが液体原料34となって析出するのを防止するための加熱手段（図示略）が設けられている。なお、輸送管53の途中部分には、酸素ガス供給源54が分岐接続され、輸送管53内に酸素ガスを供給できるように構成されている。

【0027】また、上記CVD反応装置60の底部に排気管70が設けられており、真空ポンプ71を備えた圧力調整装置72に接続されていて、CVD反応装置60の内部のガスを排気できるようになっている。更に、CVD反応装置60の基材導出部64の側方側には、CVD反応装置60内を通過する基材65を巻き取るためのテンションドラム73と巻取ドラム74とからなる基材搬送機構75が設けられている。また、基材導入部62の側部側には、基材65をCVD反応装置60に供給するためのテンションドラム76と送出ドラム77とからなる基材搬送機構78が設けられている。

【0028】次に上記のように構成された液体原料供給装置を備えた酸化物超電導体の製造装置を用いて液体原料34を気化させた原料ガスを反応チャンバ61に送り、反応チャンバ61においてテープ状の基材65上に酸化物超電導薄膜を形成し、酸化物超電導体を製造する場合について説明する。

【0029】図1に示す製造装置を用いて酸化物超電導体を製造するには、まず、テープ状の基材65と液体原料34を用意する。この基材65は、長尺のものを用いることができるが、特に、熱膨張係数の低い耐熱性の金属テープの上面にセラミックス製の中間層を被覆してなるものが好ましい。上記耐熱性の金属テープの構成材料としては、銀、白金、ステンレス鋼、銅、ハステロイ（C276等）などの金属材料や合金が好ましい。また、上記金属テープ以外では、各種ガラステープあるいはマイカテープなどの各種セラミックスなどからなるテープを用いても良い。次に、上記中間層を構成する材料は、熱膨張係数が金属よりも酸化物超電導体の熱膨張係数に近い、YSZ（イットリウム安定化ジルコニア）、$SrTiO_3$、MgO、Al_2O_3、$LaAlO_3$、$LaGaO_3$、$YAlO_3$、ZrO_2などのセラミックスが好ましく、これらの中でもできる限り結晶配向性の整ったものを用いることが好ましい。

【0030】次に酸化物超電導体をCVD反応により生成させるための液体原料34は、成膜するべき目的化合物の構成金属元素の有機金属錯体、金属アルコキシドなどの金属有機化合物を、目的化合物の組成比となるように複数種混合し、THFなどの有機溶媒に溶解させたものを用いることができる。このような液体原料34を用意したならば、収納容器40に満たしておく。

【0031】上記のテープ状の基材65を用意したならば、これを反応チャンバ61内に基材搬送機構78により基材導入部62から所定の移動速度で送り込むとともに基材搬送機構75の巻取ドラム74で巻き取り、更に反応生成室63内の基材65を加熱ヒータ47で所定の温度に加熱する。なお、基材65を送り込む前に、不活性ガス供給源68から不活性ガスをパージガスとして反応チャンバ61内に送り込み、同時に圧力調整装置72を作動させて反応チャンバ61の内部のガスを抜くことで反応チャンバ61内の空気等の不用ガスを排除して内部を洗浄しておくことが好ましい。

【0032】基材65を反応チャンバ61内に送り込んだならば、酸素ガス供給源69から反応チャンバ61内に酸素ガスを送り、更に、加圧源43ならびにMFC41aにより収納容器42から液体原料34を接続管41を経て加圧式液体ポンプ35に送液し、該加圧式液体ポンプ35により液体原料34を0.1～1.0ml／分程度の速度で毛細管31a内に圧送し、これと同時にアトマイズガスをアトマイズガス供給部32に流量200～300ccm程度で送り込むとともにシールドガスを

シールドガス供給部３３に流量２００～３００ｃｃ程度で送り込む。また、同時に圧力調整装置７２を作動させ反応チャンバ６１の内部のガスを排気する。この際、シールドガスの温度は、室温程度になるように調節しておく。また、気化器５０の内部温度が上記原料のうちの最も気化温度の高い原料の最適温度になるようにヒータ５１により調節しておく。ここで用いる毛細管３１ａとしては、液体原料３４の供給量に応じた内径を有するものを予め毛細管挿入部３１に挿入しておく。また、液体原料３４の供給量を変更する場合に備えて、内径が異なる数種類の毛細管３１ａを用意しておく。

【００３３】すると、液体原料３４は毛細管３１ａの先端に達し、この後、吐出口３１ｃから吹き出る際、アトマイズガス供給部３２から流れてくるアトマイズガスにより直ちに霧化されるので、一定流量のミスト状の液体原料３４が気化器５０内に連続的に供給される。そして、気化器５０の内部に供給されたミスト状の液体原料３４は、ヒータ５１により加熱されて気化し、原料ガスとなり、さらにこの原料ガスは輸送管５３を介してガス拡散部６６に連続的に供給される。この時、輸送管５３の内部温度が上記原料のうちの最も気化温度の高い原料の最適温度になるように上記加熱手段により調節しておく。また、この時、酸素ガス供給源５４から酸素ガスを供給して原料ガス中に酸素を混合する操作も行う。

【００３４】次に、反応チャンバ６１の内部においては、輸送管５３の出口部分からガス拡散部６６に出た原料ガスが、ガス拡散部６６から拡散しながら反応生成室６３側に移動し、反応生成室６３の内部を通り、次いで基材６５の近傍を移動してガス排気管７０に引き込まれるように移動する。従って、加熱された基材６５の上面側で原料ガスを反応させて酸化物超電導薄膜を生成させることができる。以上の成膜操作を所定時間継続して行なうことにより、基材６５上に所望の厚さの膜質の安定した酸化物超電導薄膜を備えた酸化物超電導体８０を得ることができる。

【００３５】また、液体原料３４の供給量を変更する場合、先に取り付けた毛細管３１ａが変更後の供給量に応じた内径を有していないときには、先に取り付けられている毛細管３１ａを毛細管挿入部３１から外し、変更後の供給量に応じた内径を有する毛細管３１ａを毛細管挿入部３１に挿入することにより、毛細管３１ａを容易に交換することができる。このように毛細管３１ａを交換した後は、上述の方法と同様にして酸化物超電導薄膜を成膜することができる。

【００３６】実施形態の液体原料供給装置（原料溶液供給部交換型の液体原料供給装置）３０にあっては、原料溶液供給部としての毛細管３１ａが着脱交換可能に取り付けられたことにより、液体原料３４の供給量を変更する場合、変更後の供給量に応じて毛細管３１ａのみを交換するだけで済み、よって従来のように原料溶液供給部の内径が異なる数種類の液体原料供給装置を用意する必要がなく、経済的である。また、この液体原料供給装置３０によれば、液体原料３４の供給量の変更に応じて交換される部分が毛細管３１ａだけで済み、毛細管挿入部３１ａやアトマイズガス供給部３２やシールドガス供給部３３については同じものを使用できるので、従来のように液体原料供給装置ごと交換する場合に比べて、液体原料供給装置の個体差に起因する寸法差異を低減でき、あらゆる供給量に応じて良好な液体原料の供給状況および霧化状況が再現性良く得られる。従って、このような液体原料溶液供給装置３０が備えられた酸化物超電導体の製造装置によれば、良好な酸化物超電導薄膜を再現性良く製造できる。上記実施形態においては、本発明のＣＶＤ用液体原料供給装置を酸化物超電導体の製造装置に備えた場合について説明したが、超電導体の製造装置に限らず、ＣＶＤ法により薄膜を製造する薄膜製造装置に備えられていてもよい。

【００３７】

【実施例】（実施例１）図２に示した原料溶液供給部交換型の液体原料供給装置が備えられた図１の酸化物超電導体の製造装置を用いてＹ-Ｂａ-Ｃｕ-Ｏ系の酸化物超電導体を以下のようにして作製した。液体原料として、Ｙ（ｔｈｄ）$_3$、Ｂａ（ｔｈｄ）$_2$、Ｃｕ（ｔｈｄ）$_2$をモル比でＹ：Ｂａ：Ｃｕ＝１．０：２．４：３．３で混合したものをＴＨＦ溶液に溶解した液体原料を収納容器に貯留した。この液体原料を加圧源ならびに液体微量ＭＦＣにより加圧式液体ポンプに供給し、さらに該加圧式液体ポンプから液体原料を供給速度０．２ｍｌ／分で毛細管に供給した。これと同時にアトマイズガスとしてＡｒをアトマイズガス供給部に流量３００～１０００ｃｃｍ程度で送り込むとともにシールドガスとしてＡｒをシールドガス供給部に流量１００ｃｃ程度で送り込んだ。上記毛細管としては内径が５０μｍのものを用いた。

【００３８】以上の操作により、液体原料を毛細管に良好に圧送することができ、また、毛細管に圧送された液体原料をミスト状の液体原料として気化器内に一定量連続的に供給することができ、さらにこの液体原料が気化した原料ガス（ＣＶＤガス）も反応チャンバに一定量連続的に供給することができた。この時の気化器およびＣＶＤガス輸送管の温度は２３０℃とした。反応チャンバ内の基材移動速度１．０ｍ／時間、基材加熱温度８００℃、リアクタ内圧力５トール、酸素ガス供給源からの酸素ガス流量を５０～１００ｍｌ／分に設定して、基材上に厚さ０．４～０．５μｍのＹ-Ｂａ-Ｃｕ-Ｏ系の酸化物超電導薄膜を連続的に形成し、酸化物超電導体を得た。ここでの基材としては、ハステロテープ上にイオンビームアシストスパッタリング法によりＹＳＺ（イットリウム安定化ジルコニア）面配向中間層を形成したもの（幅１ｃｍ×長さ～３０ｃｍ×厚さ０．０２ｃｍ）を用いた。

【００３９】（比較例１）原料溶液供給部交換型の液体原料供給装置に代えて従来の原料溶液供給部一体型の液体原料供給装置が備えられた酸化物超電導体の製造装置を用いる以外は上記実施例１と同様にしてY-Ba-Cu-O系の酸化物超電導体を作製した。

【００４０】実施例１ならびに比較例１で得られたテープ状の酸化物超電導体を、それぞれ酸化物超電導体の中央部分側に対し、スパッタ装置によりＡｇコーティングを施し、更に両端部側にそれぞれＡｇの電極を形成し、Ａｇコーティング後に純酸素雰囲気中にて５００℃で２時間熱処理を施して測定試料とした。そして、これら試料を液体窒素で７７Ｋに冷却し、外部磁場０Ｔ（テスラ）の条件で各試料の臨界電流密度（Ｊｃ）を測定したところ、実施例１で得られた酸化物超電導体と比較例１で得られた酸化物超電導体は、共に、３．０×10^5Ａ／ｃｍ²（７７Ｋ、０Ｔ）を確保することができた。

【００４１】（実施例２）内径１００μｍの毛細管のみ交換し、加圧式液体ポンプから毛細管に供給する液体原料の供給速度を０．６ｍｌ／分に変更した以外は上記実施例１と同様にしてY-Ba-Cu-O系の酸化物超電導体を作製した。

（比較例２）内径１００μｍの原料溶液供給部が備えられた液体原料供給装置ごと交換し、加圧式液体ポンプから原料溶液供給部に供給する液体原料の供給速度を０．６ｍｌ／分に変更した以外は上記比較例１と同様にしてY-Ba-Cu-O系の酸化物超電導体を作製した。

【００４２】実施例２ならびに比較例２で得られたテープ状の酸化物超電導体を、それぞれ酸化物超電導体の中央部分側に対し、スパッタ装置によりＡｇコーティングを施し、更に両端部側にそれぞれＡｇの電極を形成し、＊Ａｇコーティング後に純酸素雰囲気中にて５００℃で２時間熱処理を施して測定試料とした。そして、これら試料を液体窒素で７７Ｋに冷却し、外部磁場０Ｔ（テスラ）の条件で各試料の臨界電流密度（Ｊｃ）を測定したところ、比較例２で得られた酸化物超電導体は、１．０×10^5Ａ／ｃｍ²（７７Ｋ、０Ｔ）であり、比較例１で得られた酸化物超電導体よりも臨界電流密度の低下が認められ、また、超電導特性の再現性も悪いことがわかった。これに対して実施例２で得られた酸化物超電導体は、２．５×10^5Ａ／ｃｍ²（７７Ｋ、０Ｔ）であり、実施例１で得られた酸化物超電導体の臨界電流密度の値に近い値が得られており、また、超電導特性が良好な酸化物超電導体が再現性良く得ることができた。

【００４３】（実施例３）液体原料の供給速度を０．１～１．０ｍｌ／分の範囲で変更し、かつ変更後の供給量に応じて毛細管のみを交換する以外は実施例１と同様にして収納容器から送液された液体原料を加圧式液体ポンプにより毛細管内に圧送し、さらにこの毛細管に圧送された液体原料をミスト状の液体原料として気化器内に供給し、このときの液体原料の毛細管への供給状況および気化器への霧化状況について調べた。液体原料の供給速度を変更する際には、変更後の供給量に応じた内径を有する毛細管を選択し、毛細管のみ交換したところ、液体原料の供給量が０．１～１．０ｍｌ／分の範囲で全て良好な液体原料の供給状況および霧化状況を実現できた。下記表１に液体原料の供給量（ｍｌ／分）と、各供給量のときに用いた毛細管の内径（μｍ）を示す。

【００４４】

【表１】

毛細管の内径（μｍ）	５０以下	５０	７５	１００	１５０
液体原料の供給量（ｍｌ／分）	0.1-0.2	0.2-0.3	0.3-0.5	0.5-0.7	0.7以上

【００４５】

【発明の効果】以上説明したように本発明のＣＶＤ用液体原料供給装置にあっては、毛細管が着脱交換可能に取り付けられたことにより、液体原料の供給量を変更する場合、変更後の供給量に応じて毛細管のみを交換するだけで済み、よって従来のように原料溶液供給部の内径が異なる数種類の液体原料供給装置を用意する必要がなく、経済的である。また、本発明のＣＶＤ用液体原料供給装置によれば、液体原料の供給量の変更に応じて交換される部分が毛細管だけで済み、毛細管挿入部やアトマイズガス供給部やシールドガス供給部については同じものを使用できるので、従来のように液体原料供給装置ごと交換する場合に比べて、液体原料供給装置の個体差に※起因する寸法差異を低減でき、あらゆる供給量に応じて良好な液体原料の供給状況および霧化状況が再現性良く得られる。

【００４６】また、上記毛細管は着脱交換可能に取り付けられているので、目的の液体供給量に応じた毛細管を任意に選ぶことができ、選択した毛細管に交換することにより、目的の液体供給量を迅速に得ることができる。また、上記毛細管は着脱交換可能であるので、送液する液体の種類に応じた毛細管を任意に選ぶことができ、従って、あらゆる種類の液体の供給に用いることができ、しかも毛細管は容易に交換できるので、あらゆる種類の液体を迅速に供給することができる。従って、本発明のＣＶＤ用液体原料溶液供給装置が備えられた薄膜の製造

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装置によれば、良好な薄膜を再現性良く製造できる。また、本発明のＣＶＤ用液体原料溶液供給装置において、液体原料を毛細管内に加圧送液するための加圧式液体ポンプが設けられたものにあっては、内径が５０μｍ～数１５０μｍ程度と細い内径を有する毛細管内にも液体原料を良好に加圧送液することができる。

【図面の簡単な説明】

【図１】　本発明に係るＣＶＤ用液体原料供給装置を備えた酸化物超電導体の製造装置の一例を示す構成図である。

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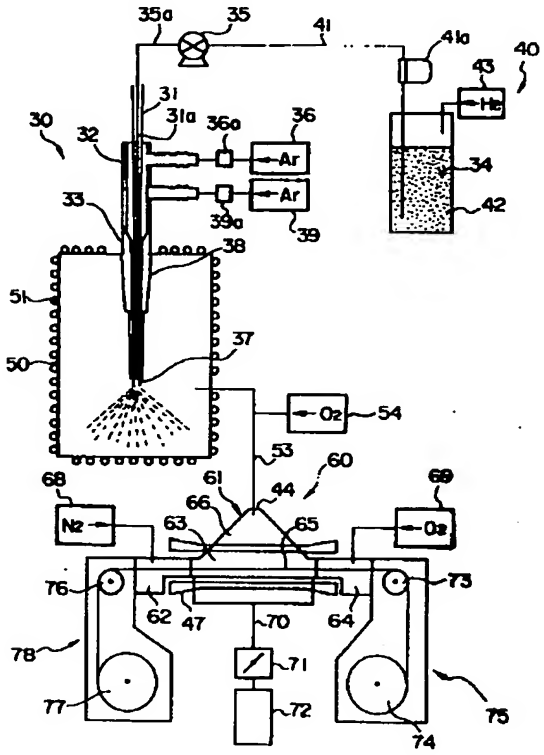
【図２】　図１の本発明に係るＣＶＤ用液体原料供給装置を示す拡大図である。

【図３】　図２のＣＶＤ用液体原料供給装置のＡ－Ａ線断面図である。

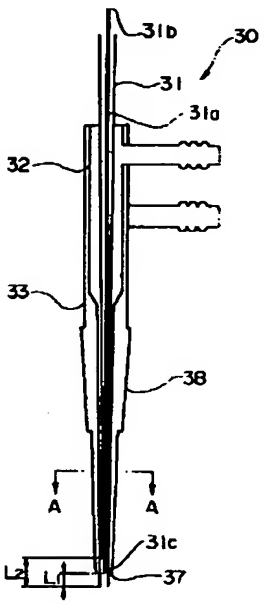
【符号の説明】

３０…液体原料供給装置、３１ａ…毛細管、３１…毛細管挿入部、３２…アトマイズガス供給部、３３…シールドガス供給部、３４…液体原料、３５…加圧式液体ポンプ。

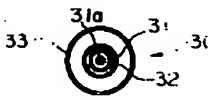
【図１】



【図２】



【図３】



フロントページの続き

(72)発明者　斉藤　隆
東京都江東区木場１丁目５番１号　株式会社フジクラ内

(72)発明者　長屋　重夫
愛知県名古屋市緑区大高町字北関山20番地の１　中部電力株式会社電力技術研究所内

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the liquid feeding equipment for CVD with which the thin film deposition system which forms oxide ingredients, such as oxides superconductors, on a base material with chemistry gaseous-phase vacuum deposition (henceforth a CVD method) is equipped.
[0002]
[Description of the Prior Art] In recent years, oxides superconductors, such as for example, a Y-Ba-Cu-O system, a Bi-Sr-calcium-Cu-O system, and a Tl-Ba-calcium-Cu-O system, are discovered for critical temperature (Tc) as oxides superconductors higher than liquid nitrogen temperature (about 77 K). And researches various for the purpose which uses these oxide superconductivity objects for fields, such as a power cable, a magnet, an energy storage, a generator, medical equipment, and a current lead, are advanced. As one of the manufacture approaches of such oxides superconductors, the approach of forming an oxide superconductivity thin film on a base material front face by thin film means forming, such as chemistry gaseous-phase vacuum deposition (CVD method), is learned. The oxide superconductivity thin film formed by this kind of thin film means forming has large critical current density (Jc), and demonstrating the outstanding superconduction property is known. Moreover, the CVD method which performs organometallic compounds, such as a metal complex and a metal alkoxide, as a raw material also in a CVD method has a quick membrane formation rate, and it is observed as a means which can form the thicker film in a short time.
[0003] As a raw material compound usually used in the manufacture approach of the oxides superconductors by such CVD method beta-diketone compound, a cyclopentadienyl compound, etc. of each element which constitute an oxide superconductivity object are used. To manufacture of the oxides superconductors of a Y-Ba-Cu-O system The organometallic complex raw material (MO raw material) of Y (thd)3, Ba (thd)2 or Ba(thd)2 and phen2, and Cu(thd)2 grade etc. is used (thd=2, 2 and 6, 6-tetramethyl - 3, 5-heptane dione). Although these organometallic complex raw materials are solid raw materials at a room temperature and by heating at 200-300 degrees C shows a high sublimation property Although presentation control is difficult since sublimation effectiveness is greatly influenced by the purity of a raw material, surface area change of the preparation raw material accompanying heating time, etc. The complex raw material of these solid-states was melted to organic solvents, such as a tetrahydrofuran (THF), isopropanol, toluene, and a jig rim (2, 5, 8-TORIOKISO nonane), and was used as a liquid raw material.
[0004] Heating evaporation is further carried out with a carburetor, these liquid raw materials are sent into a reaction chamber with carrier gas so that it may mention later, a chemical reaction is produced within this reaction chamber, and the target Y-Ba-Cu-O system oxides superconductors can be obtained by making a resultant deposit on the front face of the base material installed in the reaction chamber. By the way, when what dissolved the organometallic complex raw material in the organic solvent was used as a liquid raw material for CVD, the liquid feeding equipment for CVD had become a problem.
[0005] As a manufacturing installation of oxides superconductors equipped with the conventional liquid

feeding equipment for CVD used for manufacture of the above oxides superconductors The undiluted solution feeder which sends this raw material solution to the liquid feeding equipment for CVD while storing a liquid raw material, The liquid feeding equipment for CVD which sprays the sent liquid raw material into a carburetor, The sprayed liquid raw material is made to evaporate and the outline configuration is carried out from the carburetor which supplies this material gas in a CVD reactor while considering as material gas, and the CVD reactor made to deposit on the radical of the shape of a tape which had supplied material gas heated.

[0006] As the ** liquid feeding equipment above-mentioned [CVD], the thing of Japanese Patent Application No. No. 143738 [nine to] is proposed by invention-in-this-application persons. The tubed raw material solution feed zone by which, as for this liquid feeding equipment for CVD, a liquid raw material is supplied to the interior, The periphery of this raw material solution feed zone is surrounded, and it is prepared, and narrows the point in tubed [by which the atomize gus for atomizing the above-mentioned liquid raw material is supplied to the clearance between the above-mentioned raw material solution feed zones]. The atomize gus feed zone of **, Surround the periphery of this atomize gus feed zone, and it is prepared. It is the thing of 3 detonator structures by which an outline configuration is carried out from the tubed shielding gas feed zone by which the shielding gas which cools and shields the above-mentioned raw material solution feed zone and the above-mentioned atomize gus feed zone is supplied to the clearance between the above-mentioned atomize gus feed zones. This liquid feeding equipment for CVD is glass, the junction unification of the atomize gus feed zone and shielding gas feed zone which constitute this equipment is mutually carried out in the upper limit section, and the above-mentioned raw material solution feed zone is joined to these in one. According to the liquid feeding equipment for CVD of such a configuration, a liquid raw material with the high vapor pressure which uses THF etc. as a solvent is comparatively stabilized inside a carburetor, and continuation supply is possible.

[0007] In order to manufacture long oxides superconductors using the manufacturing installation of oxides superconductors equipped with such conventional liquid feeding equipment (liquid feeding equipment of raw material solution feed zone one apparatus) Spray into a carburetor the liquid raw material which sent the liquid raw material from the undiluted solution feeder in the raw material solution feed zone of the liquid feeding equipment for CVD, and was sent in this feed zone, the this sprayed liquid raw material is made to evaporate within a carburetor, it considers as material gas, and this material gas is supplied in a CVD reactor. It is made to run a tape-like base material in a CVD reactor with this, and long oxides superconductors are obtained by heating the base material of the shape of this tape further, and making a resultant deposit on a base material.

[0008]

[Problem(s) to be Solved by the Invention] However, it sets to the conventional liquid feeding equipment for CVD. Since the optimal bore of a raw material solution feed zone changes with amount of supply of a liquid raw material, in case it is membrane formation of an oxide superconductivity thin film Some kinds of liquid feeding equipments with which the bores of a raw material solution feed zone differ beforehand are prepared. Whenever it changed the amount of supply of a liquid raw material, the liquid feeding equipment which has the raw material solution feed zone which has the optimal bore was chosen, and when the bore of a raw material solution feed zone was unsuitable, it had to exchange the whole liquid feeding equipment, and was uneconomical. Moreover, conventional liquid feeding equipment was difficult to produce the thing of the same dimension completely, since it is handmade glassware, and since not only the tube diameter of a raw material solution feed zone but the tube diameters of an atomize gus feed zone or a shielding gas feed zone differed delicately, the supply situation of a liquid raw material changed for every equipment, and it had the problem that the repeatability of the supply situation of a liquid raw material and a atomization situation was bad. Therefore, when oxides superconductors were manufactured using the manufacturing installation of the oxides superconductors equipped with conventional liquid feeding equipment and liquid feeding equipment was exchanged, there was a problem that a good oxide superconductivity thin film was not obtained with sufficient repeatability according to the dimension error resulting from the individual

difference of this equipment.
[0009] This invention is made in view of the above-mentioned situation, and it is economical, the dimension difference resulting from the individual difference of liquid feeding equipment can be reduced, and it aims at offering the liquid feeding equipment for CVD which can improve the repeatability of the supply situation of a liquid raw material, and a atomization situation.
[0010]
[Means for Solving the Problem] The capillary tube as a raw material solution feed zone with which a liquid raw material is supplied to the interior in invention according to claim 1, The periphery of the capillary tube insertion section in which this capillary tube is inserted, and this capillary tube insertion section is surrounded, and it is prepared, and narrows the point in tubed [by which the atomize gus for atomizing the above-mentioned liquid raw material is supplied to the clearance between the above-mentioned capillary tube insertion sections]. The atomize gus feed zone of **, It comes to provide the tubed shielding gas feed zone by which the shielding gas which encloses the periphery of this atomize gus feed zone, is formed, and cools and shields the above-mentioned capillary tube, the above-mentioned capillary tube insertion section, and the above-mentioned atomize gus feed zone is supplied to the clearance between the above-mentioned atomize gus feed zones. the above-mentioned capillary tube -- attachment and detachment -- the liquid feeding equipment for CVD characterized by being inserted in the above-mentioned capillary tube insertion section exchangeable was made into the solution means of the above-mentioned technical problem.
[0011] Moreover, in invention according to claim 2, the liquid feeding equipment for CVD according to claim 1 characterized by the bore of the above-mentioned capillary tube being 50 micrometers - 150 micrometers was made into the solution means of the above-mentioned technical problem. Moreover, in invention according to claim 3, the liquid feeding equipment for CVD according to claim 1 or 2 characterized by what the pressure type liquid pump for carrying out pressurization liquid sending possesses the above-mentioned liquid raw material for in the above-mentioned capillary tube was made into the solution means of the above-mentioned technical problem.
[0012]
[Embodiment of the Invention] Hereafter, 1 operation gestalt of the liquid feeding equipment for CVD of this invention is explained using a drawing. Drawing 1 shows an example of the manufacturing installation of oxides superconductors equipped with the liquid feeding equipment for CVD concerning this invention. The outline configuration of the manufacturing installation of these oxides superconductors is carried out from the liquid feeding equipment 30 for CVD, the undiluted solution feeder 40, the carburetor 50, and the CVD reactor 60.
[0013] Capillary tube 31a as a raw material solution feed zone by which a liquid raw material is supplied to the interior as liquid feeding equipment 30 is shown in drawing 3 from drawing 2 , It narrows the point in tubed [which was prepared by surrounding the periphery of the capillary tube insertion section 31 in which capillary tube 31a is inserted, and the capillary tube insertion section 31]. The atomize gus feed zone 32 of **, An outline configuration is carried out from the tubed shielding gas feed zone 33 prepared by surrounding the periphery except the point of this atomize gus feed zone 32.
[0014] The liquid raw material 34 with which capillary tube 31a is sent in from the undiluted solution feeder 40 is supplied to the interior. As an example of the dimension of capillary tube 31a, an outer diameter is about 375 micrometers and a bore is 50 micrometers - about 150 micrometers as several 10 micrometers - about hundreds of micrometers and a more desirable bore.
[0015] the above capillary tube 31a of a configuration -- attachment and detachment -- it is inserted in the capillary tube insertion section 31 exchangeable. The capillary tube insertion section 31 is for guiding capillary tube 31a into the atomize gus feed zone 32. As for the bore of the point of the capillary tube insertion section 31, it is desirable that it is a value near the outer diameter of capillary tube 31a. As an example of the dimension of the capillary tube insertion section 31 in case the outer diameter of capillary tube 31a is 375 micrometers, it considers as the bore of 380 micrometers - about 390 micrometers, and the outer diameter of about 425-475 micrometers. Capillary tube 31a inserted into such the capillary tube insertion section 31 is connected with the undiluted solution feeder 40 mentioned

later.
[0016] it is the liquid which stores temporarily the liquid raw material 34 supplied to the center section of this capillary tube 31a -- it is desirable that the ball (illustration abbreviation) is formed. it is this liquid -- the bore of a ball is larger than the bore of liquid feed hopper 31b of the upper part of capillary tube 31a, or lower liquid feed hopper 31b, and it is continuously sent in at a tip, the liquid raw material 34 sent in from the undiluted solution feeder 40 collecting. it is such liquid -- when the ball is formed, air bubbles etc. are liquid even if air bubbles etc. are mixing into the liquid raw material 34 -- since it comes floating to the oil level of the liquid raw material 34 collected on the ball, it can prevent reaching even at a tip.
[0017] Since several 10kg/cm2 ****** is needed in order to send the liquid raw material 34 in capillary tube 31a which has the above bores of several 10 micrometers - about hundreds of micrometers, it is desirable that the pressure type liquid pump 35 for carrying out pressurization liquid sending of the liquid raw material 34 sent in from the undiluted solution feeder 40 into capillary tube 31a is connected to liquid feed hopper 31b through communication trunk 35a. If such a pressure type liquid pump 35 is formed, pressurization liquid sending of the liquid raw material 34 can be carried out by several 100kg/cm2. The undiluted solution feeder 40 mentioned later is connected to this pressure type liquid pump 35 through a communication trunk 41.
[0018] The atomize gus for atomizing the liquid raw material 34 above-mentioned [the atomize gus feed zone 32] to the clearance between the capillary tube insertion sections 31 is supplied. The atomize gus source of supply 36 is connected to the upper part of the atomize gus feed zone 32 through MFC36a for atomize gus, and it is constituted so that atomize gus can be supplied in the atomize gus feed zone 32. If the example of the atomize gus used here is specified, they will be argon gas, gaseous helium, nitrogen gas, etc.
[0019] While the shielding gas feed zone 33 cools capillary tube 31a, the capillary tube insertion section 31, and the atomize gus feed zone 32, the shielding gas for shielding a nozzle 37 is supplied to the clearance between the atomize gus feed zones 32. The taper section 38 which projects in the method of outside is formed in the downward part from the center section of the shielding gas feed zone 33. Moreover, the shielding gas source of supply 39 is connected to the upper part of the shielding gas feed zone 33 through MFC39a for shielding gas, and it is constituted so that shielding gas can be supplied in the shielding gas feed zone 33. If the example of the shielding gas used here is specified, they will be argon gas, gaseous helium, nitrogen gas, etc.
[0020] This liquid feeding equipment 30 consists of glass etc., the junction unification of the atomize gus feed zone 32 and the shielding gas feed zone 33 which constitute this equipment 30 is mutually carried out in the upper limit section, and the capillary tube insertion section 31 is further joined to these in one. And the nozzle 37 is constituted from the point of the atomize gus feed zone 32, and the point of capillary tube 31a by the liquid feeding equipment 30 of this example. The point of the atomize gus feed zone 32 is projected more slightly than the point of the shielding gas feed zone 33, and is about 1mm as a wire extension L1 here, for example. Moreover, the point of the atomize gus feed zone 32 is projected from the point of the capillary tube insertion section 31, and is about 3mm as a wire extension L2 here, for example. On the other hand, the tip of capillary tube 31a to insert is adjusted in **1mm to the point of the atomize gus feed zone 32 (+ is the case where the tip of capillary tube 31a projects from the point of the atomize gus feed zone 32, and - is the case where the tip of capillary tube 31a has withdrawn from the point of the atomize gus feed zone 32).
[0021] Although the liquid raw material 34 will reach delivery 31c of capillary tube 31a with the above liquid feeding equipments 30 of a configuration if atomize gus is sent into the atomize gus feed zone 32 with constant flow while feeding the liquid raw material 34 with constant flow in capillary tube 31a from liquid feed hopper 31b Since atomize gus flows from the tip of the atomize gus feed zone 32 of the outside at this tip In case it blows and comes out of delivery 31c, the liquid raw material 34 can be immediately atomized by the above-mentioned atomize gus, and can supply continuously the liquid raw material 34 of the shape of Myst of a constant rate in a carburetor 50. Moreover, if shielding gas is sent into the shielding gas feed zone 33 with constant flow with this, since the atomize gus feed zone 32, the

capillary tube insertion section 31, and capillary tube 31a will be cooled, it can prevent that the flowing liquid raw material 34 is also cooled and this liquid raw material 34 evaporates the inside of this capillary tube 31a on the way. It is the outside at the tip of the atomize gus feed zone 32, and since shielding gas flows from the tip of the upper shielding gas feed zone 33, it can prevent the perimeter of a nozzle 37 being shielded by this shielding gas, and the material gas which the liquid raw material 34 evaporated within the carburetor 50 adhering to a nozzle 37, and becoming a solid-state raw material and re-depositing further again.

[0022] The undiluted solution feeder 40 is connected with the communication trunk 41 equipped with MFC41a for liquid raw materials through communication trunk 35a equipped with the pressure type liquid pump 35, and it is in such capillary tube 31a of liquid feeding equipment 30. That these communication trunks 35a and 41 excelled [that] in the chemical resistance of the pipe to which the coat of the inside was carried out with the fluororesin is used. The undiluted solution feeder 40 possesses a stowage container 42 and the source 43 of pressurization, and the liquid raw material 34 is contained inside the stowage container 42. That the stowage container 42 excelled [that] in the chemical resistance of a carboy etc. is used. The above-mentioned source 43 of pressurization can discharge now the liquid raw material 34 which pressurized the inside of a stowage container 42 and was filled in the stowage container 42 with constant flow to a communication trunk 41 by supplying helium gas etc. in a stowage container 42.

[0023] The liquid raw material 34 contained by the stowage container 42 mixes two or more sorts of organic metal compounds, such as an organometallic complex of the configuration metallic element of the purpose compound which should form membranes, and a metal alkoxide, so that it may become the presentation ratio of the purpose compound, and it dissolves in an organic solvent. If the example of these organic metal compounds and an organic solvent is specified the organometallic complex of Y (thd)3 and Ba (thd)2 which are used when forming Y-Ba-Cu-O system oxides superconductors or Ba (thd)2 and phen2, and Cu(thd)2 grade (thd=2, 2 and 6, 6-tetramethyl - 3, 5-heptane dione) -- and They are organic solvents, such as a tetrahydrofuran (THF), isopropanol, toluene, and a jig rim (2, 5, 8-TORIOKISO nonane).

[0024] On the other hand, the container-like carburetor 50 is arranged under the liquid feeding equipment 30, a point is contained in this carburetor 50 from the center section of liquid feeding equipment 30, and liquid feeding equipment 30 and a carburetor 50 are connected. The heater 51 for heating the interior of a carburetor 50 is attached to the periphery section of this carburetor 50, desired temperature is made to heat and evaporate the liquid raw material 34 of the shape of Myst sprayed from the above-mentioned nozzle 37 at this heater 51, and material gas is obtained. This carburetor 50 is connected to the CVD reactor 60 through the duct 53.

[0025] This CVD reactor 60 has the reaction chamber 61 made from a quartz, and this reaction chamber 61 is the telescopic thing which closed oblong both ends, and is divided by the base material induction 62, the reaction generation room 63, and the base material derivation section 64 sequentially from the left of drawing 1 R> 1 by the septum (illustration abbreviation). Furthermore, while the introductory hole for introducing the tape-like base material 65 into the base material induction 62 is formed The derivation hole for deriving a base material 65 is formed in the base material derivation section 64. In the periphery section of an introductory hole and a derivation hole In the drawing, although omitted, the closure member which closes the clearance between each hole in the condition of passing the base material 65, and holds the base material induction 62 and the base material derivation section 64 in the airtight condition is prepared. Moreover, the gaseous diffusion section 66 of three square shapes which are open for free passage in the reaction generation room 63 is attached in the head-lining section of the reaction generation room 63.

[0026] On the other hand, in the exterior of the CVD reactor 60, the part of the reaction generation room 63 sides of the base material derivation section 64 is prepared in the wrap heating heater 47 from the part of the reaction generation room 63 sides of the base material induction 62, the base material induction 62 is connected to the inert gas source of supply 68, and the base material derivation section 64 is connected to the oxygen gas source of supply 69, respectively. Moreover, the duct 53 connected

with the carburetor 50 of material gas is connected to the gaseous diffusion section 66. The heating means (illustration abbreviation) for preventing that material gas serves as the liquid raw material 34, and deposits is formed in the perimeter of this duct 53. In addition, in the middle of the duct 53, to a part, multipoint connection of the oxygen gas source of supply 54 is carried out, and it is constituted so that oxygen gas can be supplied in a duct 53.

[0027] Moreover, the exhaust pipe 70 is formed in the pars basilaris ossis occipitalis of the above-mentioned CVD reactor 60, it connects with the pressure adjuster 72 equipped with the vacuum pump 71, and the gas inside the CVD reactor 60 can be exhausted now. Furthermore, the base material conveyance device 75 which consists of the tension drum 73 and the winding drum 74 for rolling round the base material 65 which passes through the inside of the CVD reactor 60 is formed in the side side of the base material derivation section 64 of the CVD reactor 60. Moreover, the base material conveyance device 78 which consists of the tension drum 76 and the sending-out drum 77 for supplying a base material 65 to the CVD reactor 60 is formed in the flank side of the base material induction 62.

[0028] Next, in delivery and a reaction chamber 61, an oxide superconductivity thin film is formed for the material gas which made the liquid raw material 34 evaporate using the manufacturing installation of the oxide superconductivity object equipped with the liquid feeding equipment constituted as mentioned above on the tape-like base material 65 at a reaction chamber 61, and the case where oxides superconductors are manufactured is explained.

[0029] In order to manufacture oxides superconductors using the manufacturing installation shown in drawing 1 , tape-like a base material 65 and the liquid raw material 34 are prepared first. Although a long thing can be used for this base material 65, its thing which comes to cover the interlayer made from the ceramics on the top face of a heat-resistant metal tape with a low coefficient of thermal expansion especially is desirable. As a component of the above-mentioned heat-resistant metal tape, metallic materials and alloys, such as silver, platinum, stainless steel, copper, and Hastelloy (C276 grade), are desirable. Moreover, except the above-mentioned metal tape, the tape which consists of various ceramics, such as various glass tapes or a mica tape, etc. may be used. Next, the ingredient which constitutes the above-mentioned interlayer has desirable ceramics, such as YSZ (yttrium fully stabilized zirconia), SrTiO3, MgO and aluminum 2O3 with the coefficient of thermal expansion near [metal] the coefficient of thermal expansion of an oxide superconductivity object, and LaAlO3, LaGaO3, YAlO3, ZrO2, and it is desirable to use that in which the crystal stacking tendency was ready as much as possible also in these.

[0030] Next, the liquid raw material 34 for making a CVD reaction generate oxides superconductors can mix two or more sorts of organic metal compounds, such as an organometallic complex of the configuration metallic element of the purpose compound which should form membranes, and a metal alkoxide, so that it may become the presentation ratio of the purpose compound, and what was dissolved in organic solvents, such as THF, can be used for it. If such a liquid raw material 34 is prepared, it will fill to the stowage container 40.

[0031] If the base material 65 of the shape of an above tape is prepared, while sending this in with predetermined passing speed from the base material induction 62 according to the base material conveyance device 78 in a reaction chamber 61, it will roll round on the winding drum 74 of the base material conveyance device 75, and the base material 65 in the reaction generation room 63 will be further heated to predetermined temperature at the heating heater 47. In addition, before sending in a base material 65, it is desirable to eliminate unnecessary gas, such as air in a reaction chamber 61, by sending in in a reaction chamber 61 by making inert gas into purge gas from the inert gas source of supply 68, operating a pressure adjuster 72 to coincidence, and extracting the gas inside a reaction chamber 61, and to wash the interior.

[0032] If a base material 65 is sent in in a reaction chamber 61, oxygen gas in a reaction chamber 61 from the oxygen gas source of supply 69 Delivery, Furthermore, the liquid raw material 34 is sent on the pressure type liquid pump 35 through a communication trunk 41 from a stowage container 42 by the source 43 of pressurization, and MFC41a. The liquid raw material 34 is fed in capillary tube 31a by about 0.1-1.0ml/minute in rate with this pressure type liquid pump 35. While sending atomize gus into

this and coincidence with a flow rate 200 - 300ccm extent at the atomize gus feed zone 32, shielding gas is sent into the shielding gas feed zone 33 by the flow rate of about 200-300 cc. Moreover, a pressure adjuster 72 is operated to coincidence and the gas inside a reaction chamber 61 is exhausted. Under the present circumstances, the temperature of shielding gas is adjusted so that it may become room temperature extent. Moreover, it adjusts at the heater 51 so that the internal temperature of a carburetor 50 may turn into optimum temperature of the raw material with the highest evaporation temperature of the above-mentioned raw materials. What has a bore according to the amount of supply of the liquid raw material 34 as capillary tube 31a used here is beforehand inserted in the capillary tube insertion section 31. Moreover, it has, when changing the amount of supply of the liquid raw material 34, and some kinds of capillary tube 31a from which a bore differs is prepared.

[0033] Then, the liquid raw material 34 reaches at the tip of capillary tube 31a, and since it is immediately atomized by the atomize gus which flows from the atomize gus feed zone 32 in case it blows and comes out of delivery 31c after this, the liquid raw material 34 of the shape of Myst of constant flow is continuously supplied in a carburetor 50. And the liquid raw material 34 of the shape of Myst supplied to the interior of a carburetor 50 is heated at a heater 51, is evaporated, and serves as material gas, and this material gas is further supplied to the gaseous diffusion section 66 continuously through a duct 53. At this time, it adjusts with the above-mentioned heating means so that the internal temperature of a duct 53 may turn into optimum temperature of the raw material with the highest evaporation temperature of the above-mentioned raw materials. Moreover, actuation which supplies oxygen gas from the oxygen gas source of supply 54, and mixes oxygen in material gas is also performed at this time.

[0034] Next, in the interior of a reaction chamber 61, it moves so that it moves to the reaction generation room 63 side, being spread from the gaseous diffusion section 66, and the material gas which appeared from the outlet part of a duct 53 in the gaseous diffusion section 66 may pass along the interior of the reaction generation room 63, may subsequently move near the base material 65 and may be drawn in the flueing tubing 70. Therefore, material gas can be made to be able to react by the top-face side of the heated base material 65, and an oxide superconductivity thin film can be made to generate. By carrying out predetermined time continuation and performing the above membrane formation actuation, the oxides superconductors 80 equipped with the oxide superconductivity thin film by which the membraneous quality of desired thickness was stabilized on the base material 65 can be obtained.

[0035] Moreover, when changing the amount of supply of the liquid raw material 34 and capillary tube 31a attached previously does not have the bore according to the amount of supply after modification, capillary tube 31a can be easily exchanged by removing capillary tube 31a attached previously from the capillary tube insertion section 31, and inserting in the capillary tube insertion section 31 capillary tube 31a which has a bore according to the amount of supply after modification. Thus, after exchanging capillary tube 31a, an oxide superconductivity thin film can be formed like an above-mentioned approach.

[0036] If it is in the liquid feeding equipment (liquid feeding equipment of a raw material solution feed zone exchange mold) 30 of an operation gestalt capillary tube 31a as a raw material solution feed zone -- attachment and detachment -- by having been attached exchangeable When changing the amount of supply of the liquid raw material 34, what is necessary is to exchange only capillary tube 31a according to the amount of supply after modification, and it is not necessary to prepare some kinds of liquid feeding equipments with which the bores of a raw material solution feed zone therefore differ like before, and is economical. Moreover, according to this liquid feeding equipment 30, the part for which it is exchanged according to modification of the amount of supply of the liquid raw material 34 requires only capillary tube 31a. Since the thing same about capillary tube insertion section 31a, the atomize gus feed zone 32, or the shielding gas feed zone 33 can be used Compared with the case where it exchanges the whole liquid feeding equipment like before, the dimension difference resulting from the individual difference of liquid feeding equipment can be reduced, and the supply situation and atomization situation of a good liquid raw material are acquired with sufficient repeatability according to all the amount of supply. Therefore, according to the manufacturing installation of the oxides superconductors

equipped with such a liquid raw material solution feeder 30, a good oxide superconductivity thin film can be manufactured with sufficient repeatability. In the above-mentioned operation gestalt, although the case where the manufacturing installation of oxides superconductors was equipped with the liquid feeding equipment for CVD of this invention was explained, you may prepare for the thin-film-fabrication equipment which manufactures a thin film not only with the manufacturing installation of a superconductor but with a CVD method.

[0037]

[Example] (Example 1) Using the manufacturing installation of the oxides superconductors of drawing 1 equipped with the liquid feeding equipment of the raw material solution feed zone exchange mold shown in drawing 2 , it is the following, and the oxides superconductors of a Y-Ba-Cu-O system were made and produced. The liquid raw material which dissolved in the THF solution what mixed Y (thd)3, Ba (thd)2, and Cu (thd)2 by the mole ratio Y:Ba:Cu=1.0:2.4:3.3 as a liquid raw material was stored in the stowage container. This liquid raw material was supplied to the pressure type liquid pump by the source of pressurization, and the liquid minute amount MFC, and the liquid raw material was further supplied to the capillary tube by part for speed-of-supply/of 0.2ml from this pressure type liquid pump. While sending Ar into this and coincidence with the flow rate 300 - 1000ccm extent as atomize gus at the atomize gus feed zone, Ar was sent into the shielding gas feed zone by the flow rate of about 100 cc as shielding gas. That whose bore is 50 micrometers as the above-mentioned capillary tube was used.

[0038] The liquid raw material which could feed the liquid raw material good to the capillary tube, and was fed by the capillary tube by the above actuation could be supplied to the constant-rate continuation target in the carburetor as a Myst-like liquid raw material, and the material gas (CVD gas) which this liquid raw material evaporated further was also able to be supplied to the constant-rate continuation target at the reaction chamber. Temperature of the carburetor at this time and CVD gas transport tubing was made into 230 degrees C. 800 degrees C, the reactor internal pressure of 5 torrs, and the oxygen gas flow rate from an oxygen gas source of supply were set as a part for 50-100ml/whenever [base material passing speed / in a reaction chamber / of 1.0m/hour /, and base material stoving temperature], the oxide superconductivity thin film of a Y-Ba-Cu-O system with a thickness of 0.4-0.5 micrometers was continuously formed on the base material, and oxides superconductors were obtained. as a base material here -- a lotus -- what formed the YSZ (yttrium fully stabilized zirconia) plane orientation interlayer by the ion beam assistant sputtering method on TEROTEPU (0.02cm in width-of-face [of 1cm] x die-length - 30cmx thickness) was used.

[0039] (Example 1 of a comparison) The oxides superconductors of a Y-Ba-Cu-O system were produced like the above-mentioned example 1 except using the manufacturing installation of the oxides superconductors which it replaced with the liquid feeding equipment of a raw material solution feed zone exchange mold, and were equipped with the liquid feeding equipment of conventional raw material solution feed zone one apparatus.

[0040] Ag coating was performed for the oxides superconductors of the shape of a tape acquired in the example 1 and the example 1 of a comparison with the sputtering system to the central part side of an oxide superconductivity object, respectively, and the electrode of Ag was further formed in the both-ends side, respectively, and after Ag coating, in the pure oxygen ambient atmosphere, heat treatment was performed at 500 degrees C for 2 hours, and it considered as the test portion. And when these samples were cooled to 77K by liquid nitrogen and the critical current density (Jc) of each sample was measured on condition that external magnetic field 0T (tesla), both the oxides superconductors obtained in the example 1 and the oxides superconductors obtained in the example 1 of a comparison were able to secure 3.0x105 A/cm2 (77K, 0T).

[0041] (Example 2) Only the capillary tube with a bore of 100 micrometers was exchanged and the oxides superconductors of a Y-Ba-Cu-O system were produced like the above-mentioned example 1 except having changed into a part for 0.6ml/the speed of supply of the liquid raw material supplied to a capillary tube from a pressure type liquid pump.

(Example 2 of a comparison) It exchanged the whole liquid feeding equipment equipped with the raw material solution feed zone with a bore of 100 micrometers, and the oxides superconductors of a Y-Ba-

Cu-O system were produced like the above-mentioned example 1 of a comparison except having changed into a part for 0.6ml/the speed of supply of the liquid raw material supplied to a raw material solution feed zone from a pressure type liquid pump.

[0042] Ag coating was performed for the oxides superconductors of the shape of a tape acquired in the example 2 and the example 2 of a comparison with the sputtering system to the central part side of an oxide superconductivity object, respectively, and the electrode of Ag was further formed in the both-ends side, respectively, and after Ag coating, in the pure oxygen ambient atmosphere, heat treatment was performed at 500 degrees C for 2 hours, and it considered as the test portion. And when these samples were cooled to 77K by liquid nitrogen and the critical current density (Jc) of each sample was measured on condition that external magnetic field 0T (tesla), the oxides superconductors obtained in the example 2 of a comparison were 1.0x105 A/cm2 (77K, 0T), and the fall of critical current density was accepted rather than the oxides superconductors obtained in the example 1 of a comparison, and they were understood that the repeatability of a superconduction property is also bad. On the other hand, the oxides superconductors obtained in the example 2 were 2.5x105 A/cm2 (77K, 0T), the value near the value of the critical current density of the oxides superconductors obtained in the example 1 is acquired, and oxides superconductors with a good superconduction property were able to obtain them with sufficient repeatability.

[0043] The speed of supply of a liquid raw material is changed in the 0.1-1.0ml range for /. (Example 3) And the liquid raw material sent from the stowage container like the example 1 is fed in a capillary tube with a pressure type liquid pump except exchanging only capillary tubes according to the amount of supply after modification. The liquid raw material furthermore fed by this capillary tube was supplied in the carburetor as a Myst-like liquid raw material, and it investigated about the supply situation to the capillary tube of the liquid raw material at this time, and the atomization situation to a carburetor. When changing the speed of supply of a liquid raw material, and the capillary tube which has a bore according to the amount of supply after modification was chosen and only capillary tubes were exchanged, the amount of supply of a liquid raw material has realized the supply situation and atomization situation of a good liquid raw material altogether in the 0.1-1.0ml range in which it is part for /. The amount of supply (a part for ml/) of a liquid raw material and the bore (micrometer) of the capillary tube used at the time of each amount of supply are shown in the following table 1.

[0044]

[Table 1]

毛細管の内径（μm）	50以下	50	75	100	150
液体原料の供給量（ml／分）	0.1-0.2	0.2-0.3	0.3 0.5	0.5-0.7	0.7以上

[0045]

[Effect of the Invention] if it is in the liquid feeding equipment for CVD of this invention as explained above -- a capillary tube -- attachment and detachment -- when changing the amount of supply of a liquid raw material by having been attached exchangeable, what is necessary is to exchange only capillary tubes according to the amount of supply after modification, and it is not necessary to prepare some kinds of liquid feeding equipments with which the bores of a raw material solution feed zone therefore differ like before, and is economical. Moreover, since according to the liquid feeding equipment for CVD of this invention the part for which it is exchanged according to modification of the amount of supply of a liquid raw material requires only a capillary tube and can use the same thing about the capillary tube insertion section, an atomize gus feed zone, or a shielding gas feed zone Compared with the case where it exchanges the whole liquid feeding equipment like before, the

dimension difference resulting from the individual difference of liquid feeding equipment can be reduced, and the supply situation and atomization situation of a good liquid raw material are acquired with sufficient repeatability according to all the amount of supply.

[0046] moreover, the above-mentioned capillary tube -- attachment and detachment -- since it is attached exchangeable, the target liquid amount of supply can be quickly obtained by being able to choose the capillary tube according to the target liquid amount of supply as arbitration, and exchanging for the selected capillary tube. moreover, the above-mentioned capillary tube -- attachment and detachment -- since the capillary tube according to the class of liquid which sends the liquid since it is exchangeable can be chosen as arbitration, therefore it can use for supply of all kinds of liquid and capillary tubes can moreover be exchanged easily, all kinds of liquid can be supplied quickly. Therefore, according to the manufacturing installation of the thin film with which it had the liquid raw material solution feeder for CVD of this invention, a good thin film can be manufactured with sufficient repeatability. Moreover, in the liquid raw material solution feeder for CVD of this invention, if it is in some in which the pressure type liquid pump for carrying out pressurization liquid sending of the liquid raw material into a capillary tube was formed, a bore can carry out pressurization liquid sending of the liquid raw material good also into the capillary tube which has 50 micrometers - about 150 micrometers of numbers, and a thin bore.

[Translation done.]